

Effects of transient thermal shock loadings on the structure of zirconia ceramics

E A Derkach^{1,2}, S P Buyakova^{1,2,3} and S N Kulkov^{1,2,3}

¹ National Research Tomsk Polytechnic University, 30 Lenin ave., 634050, Tomsk, Russia

² Institute of Strength Physics and Materials Science SB RAS, 2/4 pr. Akademicheskii, 634055, Tomsk, Russia

³ National Research Tomsk State University, 36 Lenin ave., 634050, Tomsk, Russia

E-mail: eadtomsk@yandex.ru

Abstract. In this paper the influence of thermal shock loadings on the phase composition and microstructure of $ZrO_2(Y_2O_3)$ and $ZrO_2(MgO)$ ceramics was studied. It was found that thermal shock strains were no effect on phase composition of $ZrO_2(Y_2O_3)$ ceramics. Reducing the concentration of high-temperature tetragonal t- ZrO_2 and cubic c- ZrO_2 modifications and rising the content of low-temperature monoclinic m- ZrO_2 crystal system with increasing the number of thermal shock strains were observed. The values of region coherent X-ray scattering of $ZrO_2(Y_2O_3)$ ceramics didn't changed, while the crystallite size of $ZrO_2(MgO)$ ceramics decreased. The formation of block structure in all studied ceramics was observed, the sizes of the blocks formed in the $ZrO_2(Y_2O_3)$ and $ZrO_2(MgO)$ ceramics were slightly different. The formation of the blocks in $ZrO_2(Y_2O_3)$ ceramics occurred on the grain boundaries, while the crystallites in $ZrO_2(MgO)$ ceramics were crushed due to phase transformation.

1. Introduction

The impetuous progress of high temperature technics needs to develop new materials for providing effective thermal insulation, both stable heat flux and under temperature extremes. In terms of thermal insulation characteristics, special attention is given to the zirconia based ceramics, which have an abnormally low for ceramic materials thermal conductivity ($\lambda = 1.7 - 2.0 \text{ W} / (\text{m} \cdot \text{K})$), and a high melting point ($mp = 2715 \text{ }^\circ\text{C}$). Resistance to thermal shock strains is not a fundamental characteristic and it largely depends on the structure and composition of the product. Zirconia exists in three polymorphic modifications: the low-temperature stable monoclinic m- ZrO_2 , the high-temperature tetragonal t- ZrO_2 and the high-temperature cubic c- ZrO_2 . In terms of exploitation the main attention is given to two high-temperature modifications. They are obtained by creating an interstitial solid solution of oxide materials such as MgO, Y_2O_3 , CaO, CeO_2 and others, which prevent a phase transformation during cooling process. Stabilized by different modifying additives, ceramics have differences not only in chemical composition, but also in mechanical and physical properties. Though the investigation of thermal shock resistance of zirconia-based ceramics began many years ago [1 - 7], but today the effect of thermal shock strains on the microstructure of the material was not fully defined. Gaining knowledge about the influence of the thermal shock loadings on the ceramic's structure enables to control its thermal shock resistance at the micro scale. Thereby, the aim of this work is to study the effect of thermal shock strains on the behavior of zirconia-based ceramics stabilized 5 mol. % yttria and 8.6 mol. % magnesia.



2. Materials and methods

As samples to study we used ceramic materials obtained by sintering zirconia partially stabilized 5 mol. % yttria $ZrO_2(Y_2O_3)$ and 8.6 mol. % magnesia $ZrO_2(MgO)$ powders. Studied samples had a cylindrical form. Thermal shock loading carried on cooling specimens in water from 1000 °C to 20 °C. Totally we had nine thermal shock strains. Analysis of the microstructure of the ceramics was carried out on the polished surfaces of samples by optical microscopy. Phase composition was studied using XRD analysis in the diffraction angle range from 25 to 100°, obtained with the filtered $CuK\alpha$ radiation.

Calculation of the size of coherent X-ray scattering was carried out with broadenings of X-ray reflections by:

$$D = \frac{\lambda_p}{\Delta B \cos \theta},$$

where λ_r – X-ray wavelength, ΔB – width of the X-ray reflections at half height, θ – angle of X-ray diffraction. Measuring of block sizes was carried out using random cross-sections method, the number of measurements was at least 300.

3. Results and discussion

An x-ray analysis (Figure 1) showed that the of $ZrO_2(MgO)$ ceramics was represented by two high-temperature structural modifications: tetragonal t- ZrO_2 and cubic c- ZrO_2 . Phase composition of ZrO_2

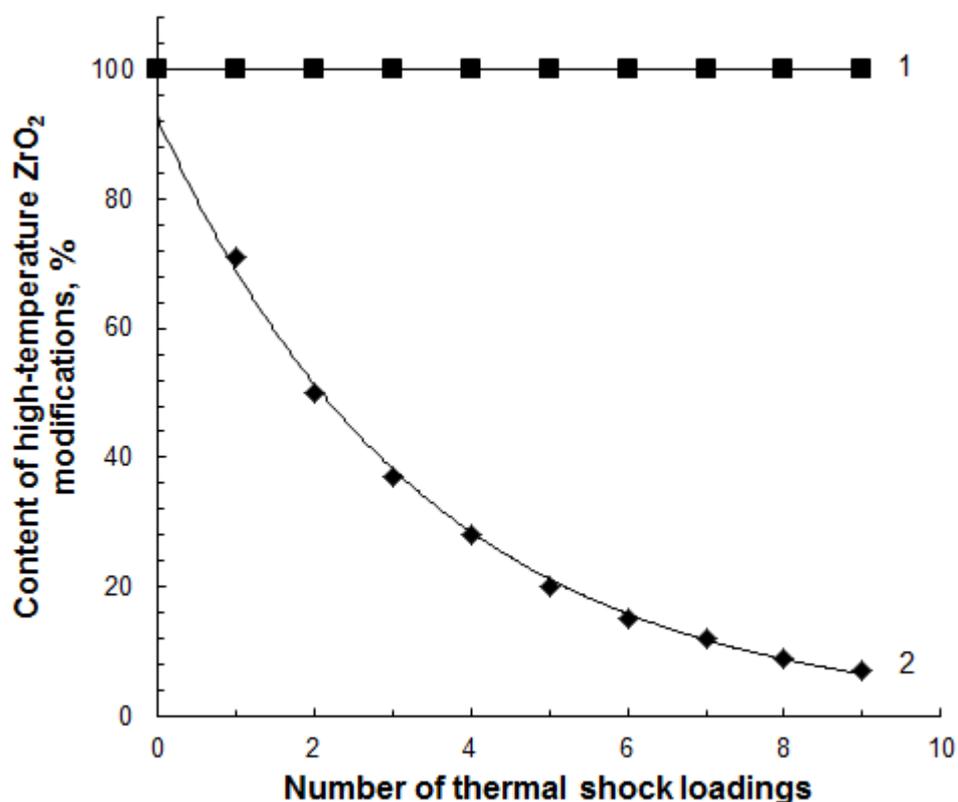


Figure 1. Dependencies of contents of high-temperature modifications: 1) t- ZrO_2 in the $ZrO_2(Y_2O_3)$ ceramics and 2) t- ZrO_2 and c- ZrO_2 in the $ZrO_2(MgO)$ ceramics vs. the number of thermal shock loadings.

(Y_2O_3) ceramics was represented only by the tetragonal t- ZrO_2 modification. Other X-ray diffraction reflections were not observed.

An analysis of the phase composition of the studied samples after thermal shock strains showed that phase composition of $ZrO_2(Y_2O_3)$ ceramics was unchanged, regardless of the number of thermal shock

loadings. The X-ray reflections showed only tetragonal t-ZrO₂ zirconia. However, in the ZrO₂(MgO) ceramics occurred decrease in the proportion of high-temperature t-ZrO₂ tetragonal and cubic-ZrO₂ phases and increasing proportion of monoclinic m-ZrO₂ phase with increasing number of thermal shock loadings. One of the reasons of increasing in the proportion of monoclinic m-ZrO₂ modification may be the disintegration of the solid solution ZrO₂-MgO, accompanied by the release of Mg²⁺ cations during the process of thermal stresses.

Calculating of the size of coherent diffracting domain (CDD) by the broadening of X-ray reflections (Figure 2) showed that this value for ZrO₂(Y₂O₃) ceramics was 63 ± 3 nm and remained unchanged

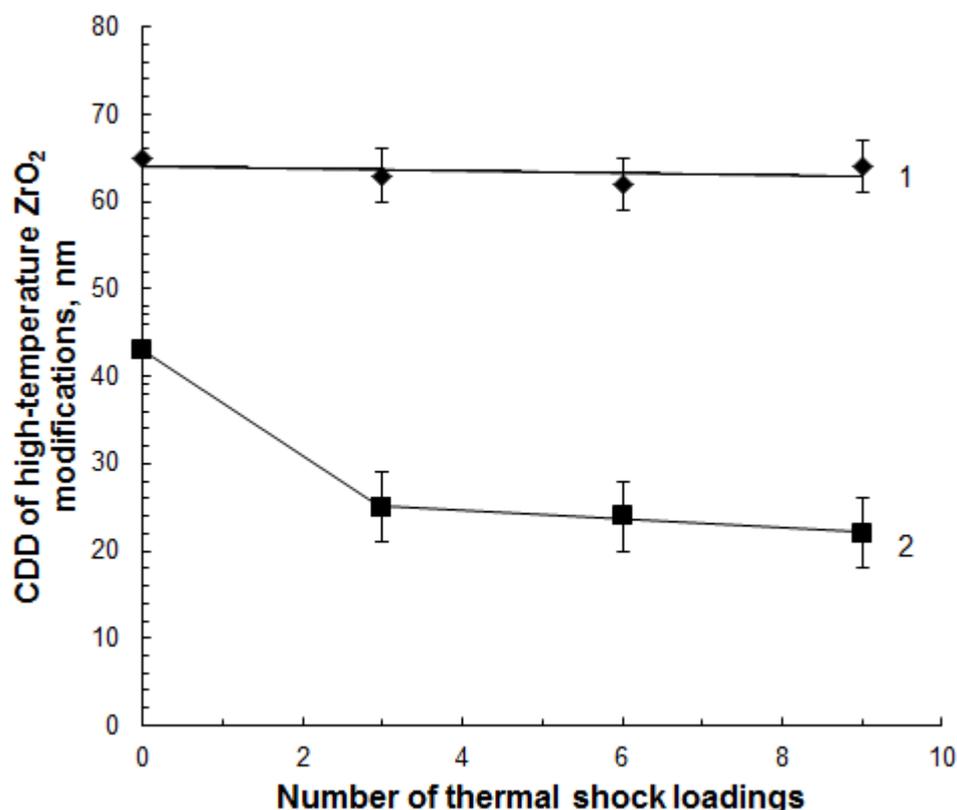


Figure 2. Dependencies of CDD of high-temperature: 1) t-ZrO₂ in the ZrO₂(Y₂O₃) ceramics and 2) c-ZrO₂ in the ZrO₂(MgO) ceramics vs. the number of thermal shock loadings.

irrespective of the number of thermal shock loadings. CDD values of ZrO₂(MgO) ceramics before thermal shock loadings were 43 ± 5 nm and after three thermal shocks we observed a decrease in size up to 25 ± 5 nm. Resizing can be associated with increasing in the proportion of monoclinic m-ZrO₂ phase. As is known the phase transformation from the high-temperature cubic c-ZrO₂ modification to the low-temperature monoclinic m-ZrO₂ phase is accompanied by significant compressive stresses due to increasing of the unit cell volume.

Figure 3 shows images of the ZrO₂(Y₂O₃) sample's surfaces before and after nine thermal shocks. It was detected the formation of a block structure, which is generated in the process of thermal shock loadings as a consequence of the formation of cracks due to the interaction of compressive and tensile stresses during the quench. This effect occurred in studied specimens in different ways. Barely visible cracks appeared on the surface of the ZrO₂(Y₂O₃) ceramics after the first thermal stress; after the third thermal shock we detected a clear boundaries of the blocks. The subsequent thermal shock loadings led to the production of new cracks in the already formed blocks: the structure was further fragmented. Growth and extension of cracks occurred on the grain boundaries. After nine thermal stresses the average block size decreased from 314 ± 26 to 268 ± 23 μm (Figure 4). Formation of the block structure in ZrO₂(MgO) ceramics occurred in differ way: fragmentary structure with average size 289

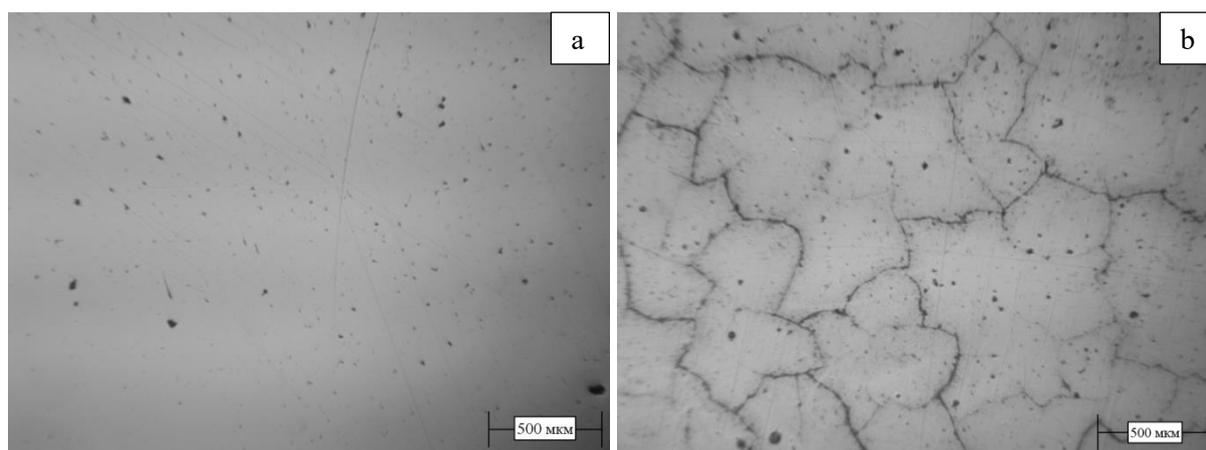


Figure 3. The images of the surfaces of $ZrO_2(Y_2O_3)$ ceramics (a) before and (b) after thermal shock loadings.

$\pm 29 \mu m$ was detected after the first thermal shock. Subsequent thermal loading was no result in further fragmentation of the surface. Moreover the samples were not destroyed despite the appearance of cracks.

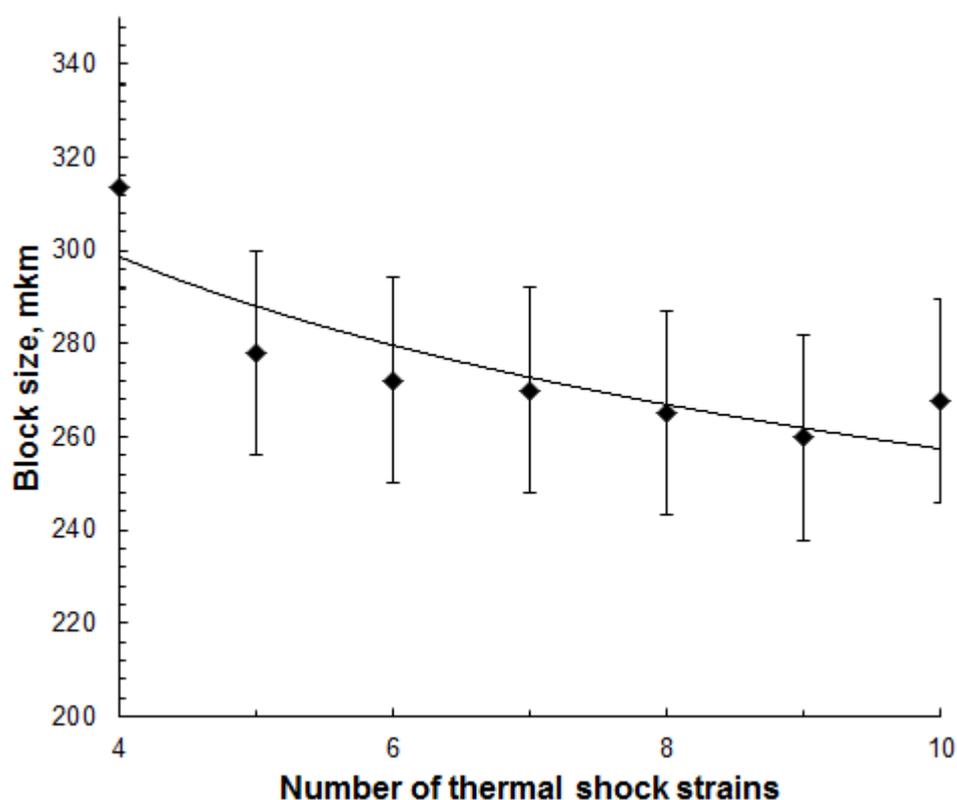


Figure 4. Dependencies of block size in $ZrO_2(Y_2O_3)$ ceramics vs. the number of thermal shock loadings.

4. Conclusion

Thus, it was found that $ZrO_2(Y_2O_3)$ ceramics retained the tetragonal crystal system $t-ZrO_2$ during all thermal shock loadings rather than $ZrO_2(MgO)$ ceramics. In $ZrO_2(MgO)$ ceramics we detected a gradual decline in concentration of high-temperature tetragonal $t-ZrO_2$ and cubic $c-ZrO_2$ phases at the

same time with appearance and increment of low-temperature m-ZrO₂ phase with increasing the number of thermal shock strains. For ZrO₂(Y₂O₃) CDD values remained unchanged, while for ZrO₂(MgO) ceramics crystallite size decreased. Formation of the block structure was observed in all studied ceramics, the sizes of the formed blocks in ZrO₂(Y₂O₃) and ZrO₂(MgO) ceramics were slightly different. The appearance of blocks in ZrO₂(Y₂O₃) ceramics occurred on the grain boundary, while in ZrO₂(MgO) ceramics crystallites were crushed due to phase transformations.

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